

POLYMERIZATION STUDIES LEADING TO
HIGH STRENGTH CHEMICAL RESISTANT ELASTOMERS
SERVICEABLE AT TEMPERATURE EXTREMES

SEMIANNUAL REPORT No. 4

by

D. I. Relyea
H. P. Smith
A. N. Johnson

December 1966

Contract No. DA19-129-AMC-487(N)

TECHNICAL REPORT

U. S. ARMY NATICK LABORATORIES
NATICK, MASSACHUSETTS

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UNIROYAL
UNITED STATES RUBBER COMPANY
RESEARCH CENTER
WAYNE, NEW JERSEY 07470

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for the period
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FOREWORD

This report was prepared by the UniRoyal United States Rubber Company under Contract No. DA-19-129-AMC-487(N) for the U. S. Army Natick Laboratories with Mr. C. B. Griffis as Project Officer. This is the fourth Semiannual Report under this contract and covers the period June 1, 1966 through November 30, 1966. This four-year contract has now reached the halfway mark.

During the six-month period covered by this report, the following manhours were expended on this project:

Senior Research Scientist	122
Research Scientists	1224
Technician (Sub-professional)	<u>960</u>
Total direct labor	2306 manhours

The technical effort for the past six months slightly exceeded the effort required by the contract and brought the total manhours for the first two years to 8955. This figure is within 1% of the prorated 9000 contract requirement. We plan to spend 2300 manhours during the next six months.

SUMMARY

1. 1,1-Difluoroallene was prepared and its polymerization and copolymerization with allene studied using a variety of catalysts. The polymers are generally of a resinous nature.
2. Copolymerizations of 1,1,2-trifluorobutadiene with butadiene or butadiene and ethylene were carried out with several catalysts, including some shown to be effective in butadiene-ethylene copolymerization. The polymeric products obtained with titanium-based anionic coordination catalysts contained only small amounts of combined fluorine. Cationically initiated copolymers with isobutylene or methyl vinyl ether contained relatively large amounts of fluorine. Preliminary measurements have been made to relate the feed ratio of monomers to the ratio of combined monomers in the polymer for some of these systems. The anionic initiators studied so far have given only low conversions to polymer.
3. Other compounds prepared for polymerization studies were 5,5,5-trifluoro-4-(trifluoromethyl)-1,3-butadiene and 4,5-bis(trifluoromethyl)cyclohexene, a precursor of 2,3-bis(trifluoromethyl)butadiene. Preliminary polymerization experiments with the first compound have given a low molecular weight polymer using a titanium-based catalyst.
4. 2,3,3,4,4-Pentafluorocyclobutene was prepared and used in unsuccessful attempted polymerizations with molybdenum- and tungsten-based ring-opening catalysts.
5. A sample of pentafluorobenzenesulfonyl chloride-cis-polybutadiene adduct was furnished to U. S. Army Natick Laboratories for evaluation. The promising test results have led to the preparation of several related adducts and of an adduct of nitrosyl fluoride-hydrogen fluoride complex with cis-polybutadiene.

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INTRODUCTION

This is the fourth semiannual report of research on the polymerization of fluorinated monomers to form random or stereospecific high polymers. This work, sponsored by the U. S. Army Natick Laboratories, has the objective of preparing new elastomeric materials which will be both oil- and chemical-resistant and have useful rubbery properties over a wide range of temperatures such as -65° to $+300^{\circ}\text{C}$.

Much of our effort during the period covered by this report has been directed to polymerization and copolymerization of conjugated dienes using a variety of anionic, cationic and anionic coordination catalysts. A start has been made at determining the relation of feed ratio to ratio of combined monomers under some of these conditions. A smaller effort has been directed to preparation and study of polymerization of some fluoromonomers new to this program, such as 1,1-difluoroallene and 2,3,3,4,4-pentafluorocyclobutene. Finally some additional work has been done to follow up the observation that improved oil-resistant and low-temperature properties can be obtained by the chemical modification of hydrocarbon polymers.

DISCUSSION

1. Introduction

In our search for novel fluorine-containing polymers with extreme-temperature utility and oil- or chemical-resistance we have continued to explore combinations of polymerization catalysts and fluorine-containing monomers. During the period covered by this report the following types of polymerization systems have been studied:

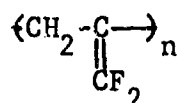
<u>Monomer</u>	<u>Catalyst</u>
1,1-Difluoroallene	Ni(0) complex
Fluorinated olefin and/or diene	Anionic coordination, e.g. $\text{TiX}_4 + \text{Al}(\text{i-Bu})_3$
Fluorinated cyclobutene	Mo or W ring-opening catalyst
Fluorinated diene	Cationic, e.g. AlBr_3
Fluorinated diene	Anionic, e.g. LiBu

Monomer syntheses where required and results of polymerization experiments are discussed below for each of these system types.

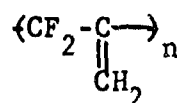
In addition, some further results are reported in the chemical modification of the readily available polymer cis-polybutadiene to provide elastomers having improved chemical and physical properties.

2. Preparation and Polymerization of 1,1-Difluoroallene

A novel fluorine-containing polymer (such as 1 or 2) might be prepared by the polymerization of 1,1-difluoroallene (3) with a nickel(0) catalyst which

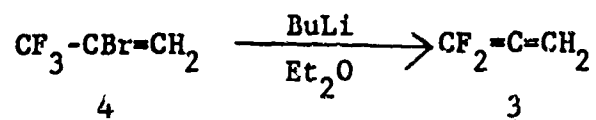


1



2

has recently been reported to polymerize allene¹. Professor Tarrant's observations on the thermal instability of 3 indicated that it would not survive as monomer during shipment. Therefore Professor Tarrant furnished as the precursor 2-bromo-3,3,3-trifluoropropene-1 (4) which we dehalogenated by the reaction:



The product (3) has a boiling point sufficiently close to the ether solvent so that purification by distillation is difficult. Hence the product was obtained as an ether solution which is suitable for use with a nickel(0) catalyst but not with such anionic coordination catalysts as the $\text{TiCl}_4\text{-Al}(\text{i-Bu})_3$ pair. It is planned to repeat the dehalogenation in a higher-boiling ether so that ether-free 3 may be obtained by distillation.

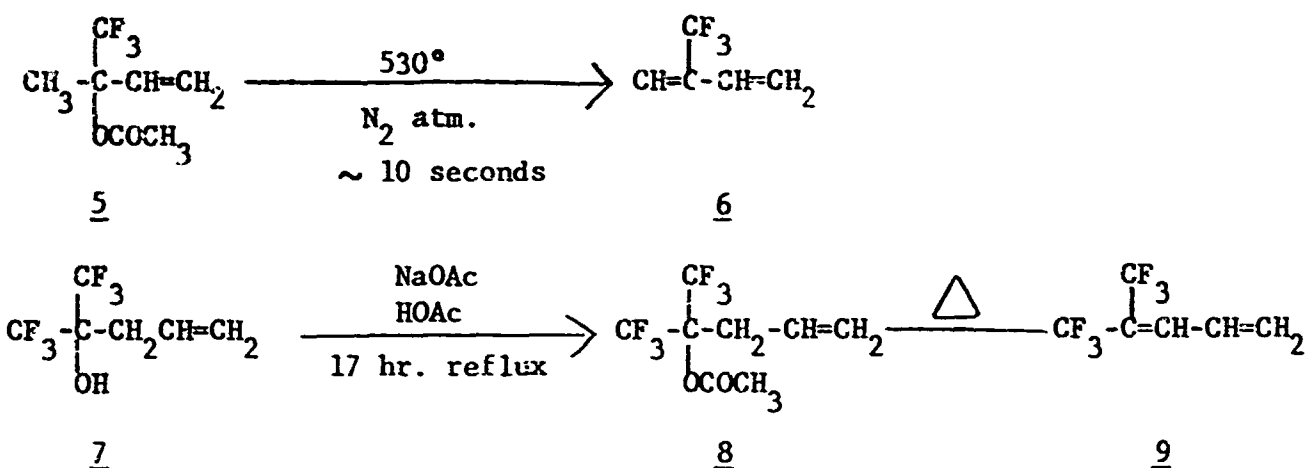
The ether solution of 1,1-difluoroallene was used in several exploratory homopolymerizations (Table I). The highest conversion to polymer (40%) was obtained in an azobisisobutyronitrile-promoted free radical polymerization (one week at 50°). Lower conversions (15%) were observed in a thermal polymerization (one week at 50°) or in a boron trifluoride-promoted polymerization (one week at -80°). Only 3% solids were obtained in a *t*-butylmagnesium chloride-promoted reaction. All of the polymers showed only weak infrared absorption at 1760 cm^{-1} , indicating few, if any, pendant =CF_2 groups along the chain (structure 1). Possible structures for the polymer include 2 or a repeating cyclopropane unit.

Table II describes the homopolymerization of 1,1-difluoroallene and its copolymerization with allene, both promoted by nickel(0) bis(1,5-cyclooctadiene). Both proceeded readily to give 81% conversion to resins. A homopolymerization of allene under the same conditions gave only 17% conversion to a resinous polymer. An analogous series of polymerizations initiated with $\text{VOCl}_3\text{-Al}(\text{i-Bu})_3$ gave dark resins. The color may possibly be the result of dehydrohalogenation of the polymer. This effect has been previously noted in polymerizations of vinyl chloride with VOCl_3 as a catalyst component².

It appears that a polymer prepared from allenes as the sole monomers has a chain too rigid to allow rubbery properties. Copolymerization of allenes with dienes will be considered as a route to rubbery polymers.

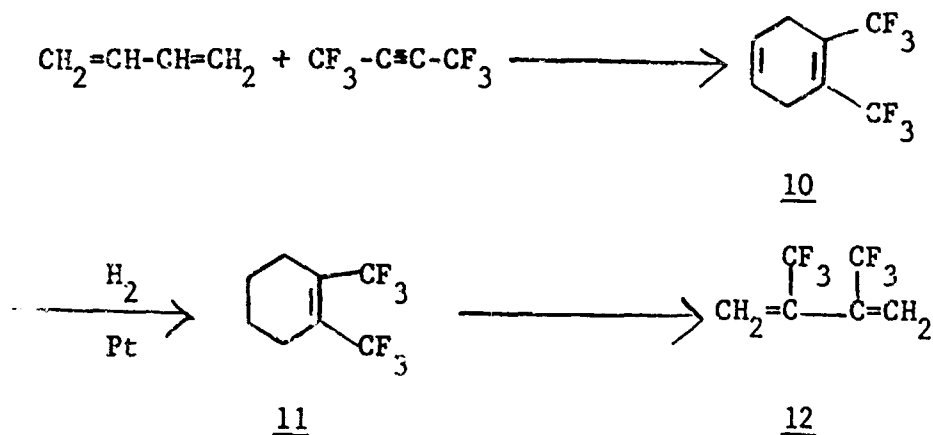
3. Preparation of Fluorinated Dienes

Two butadienes substituted with trifluoromethyl groups were prepared by the following routes from intermediates furnished by Professor Tarrant.



The yields of 6 and 9 in the pyrolysis steps were 32% and 62%, respectively. Unsuccessful attempts were made to dehydrate 7 by passage through activated alumina at 270-280° and by a phenyl isocyanate-promoted elimination.

The synthesis of 2,3-bis(trifluoromethyl)butadiene (12) was begun using a sequence of reactions described by Putnam, Harder and Castle³.



The intermediate 10 was obtained in good yield and high purity. Partial hydrogenation of 10 to 11 over platinum catalyst was accompanied by significant yields of aromatized product, o-bis(trifluoromethyl)benzene. The extent of aromatization can be decreased by the use of solvent (tetrahydrofuran) or by decreasing the ratio of catalyst to diene. Pyrolysis of the monoolefin 11 will be carried out during the period covered by our next report.

4. Polymerizations of Fluorinated Olefins and/or Dienes

a. With Anionic Coordination Catalysts

Our previous report⁴ described the formation of a rubbery terpolymer of ethylene, propylene and 2,3-bis(trifluoromethyl)norbornadiene using a catalyst composed of vanadium oxychloride and sesquiethyl aluminum sesquichloride. Some additional copolymerizations have now been carried out with butadiene and ethylene to select catalyst systems useful in preparing terpolymers containing a fluorinated monomer. These experiments are summarized in Table III. The more promising catalysts are seen to be $\text{TiI}_4\text{-Al}(\text{i-Bu})_3$ (at a 1:4.5 ratio) and $\text{TiCl}_4\text{-Al}(\text{i-Bu})_3$ (at a 1:1.4 ratio) essentially confirming prior literature observations concerning olefin polymerizations. The titanium chloride system was further examined in polymerizations of butadiene and isoprene. It was found that that higher ratios of $\text{Al}(\text{i-Bu})_3$ to TiCl_4 (at least 1.4:1) led to higher conversions to polymer and higher cis contents.

Several orientation experiments were carried out to establish the catalyst component ratios most favorable to high conversion and high cis content in polymerization of butadiene. The catalyst systems investigated were:

1. $\text{TiCl}_4\text{-Al}(\underline{i}\text{-Bu})_3$
2. $\text{TiCl}_4\text{-I}_2\text{-Al}(\underline{i}\text{-Bu})_3$
3. $\text{TiCl}_4\text{-I}_2\text{-Ti}(\text{OBr})_4\text{-Al}(\underline{i}\text{-Bu})_3$
4. $\text{Co}(\text{OCOC}_7\text{H}_{15})_2\text{-Et}_3\text{Al}_2\text{Cl}_3$
5. $\text{Co}(\text{OCOC}_7\text{H}_{15})_2\text{-EtBuAlCl}$

In general, high Al:Ti ratios (as high as 8:1 in the case of the iodine-containing catalysts) gave the best conversions and highest cis contents. With systems 2 and 3 some difficulty was had with iodine persisting through the polymer isolation treatment.

The results of these orientation experiments were then used as a guide to catalyst selection for the following polymerizations:

Butadiene and 1,1,2-trifluorobutadiene copolymerization

Ethylene-butadiene-1,1,2-trifluorobutadiene terpolymerization

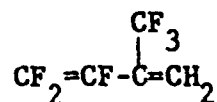
5,5,5-Trifluoro-4-(trifluoromethyl)butadiene homopolymerization

5,5,5-Trifluoro-4-(trifluoromethyl)butadiene-butadiene copolymerization

Attempts to copolymerize 1,1-trifluorobutadiene with either butadiene (Table IV) or butadiene + ethylene (Table V) using the titanium tetra-halide-aluminum triisobutyl catalysts led to polymers containing only low amounts of combined fluorodiene. Each terpolymerization experiment with the titanium tetraiodide catalysts gave two resinous catalysts which differed in their ethylene content.

Greater success was had in the use of the titanium tetraiodide catalyst for polymerization of diene 9 ("1,1-bis(trifluoromethyl)butadiene"). As Table VI shows, the copolymerization of 9 with butadiene gave 16% conversion to low molecular weight polymer. The cobalt octoate-based polymer was less effective in copolymerization. The homopolymerization proceeded best with the tetrabutyl titanate-based catalyst.

It appears that the dienes which offer the greatest likelihood of polymerizing in a 1,4-fashion are those with roughly balanced amounts of deactivation of the two double bonds. Hence, further diene polymerizations will be directed toward the use of 12 and 13.



13

The Ni(0) catalyst prepared for polymerization of allene was also tested with 1,1,2-trifluorobutadiene and several haloolefins. The products, which are described in Table VII, are all either resinous or mixtures of resins and catalyst residues.

b. With Anionic and Cationic Catalysts

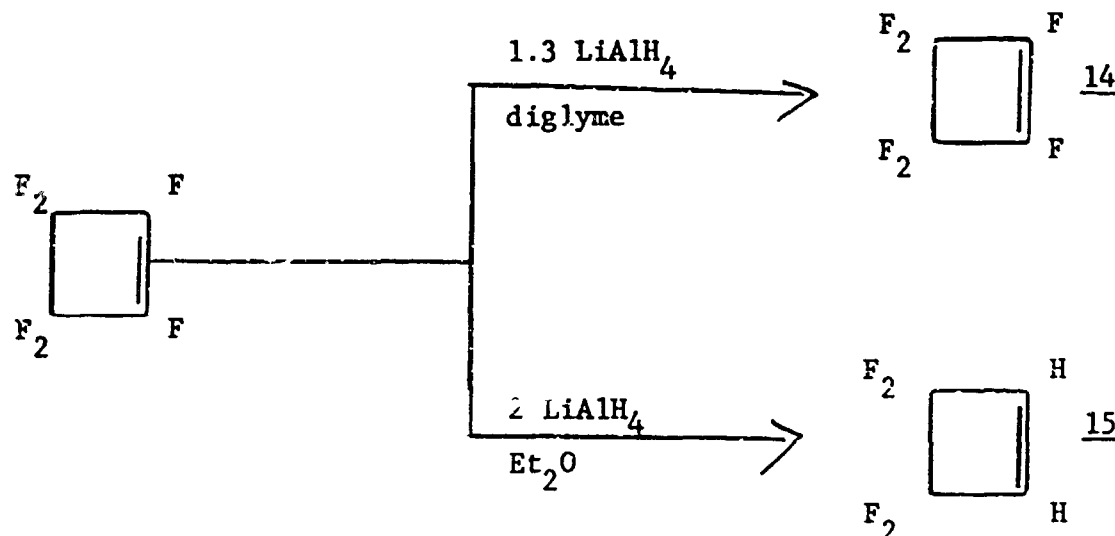
Additional experiments were carried out to explore the possibility of cationic or anionic polymerization of the fluoromonomers available to us. These experiments, summarized in Tables VIII, IX and X, indicate that the anionic initiators examined (lithium butyl, t-butylmagnesium chloride) are not effective in promoting polymerization of 1,1,2-trifluorobutadiene or its copolymerization with butadiene. Certain comonomer-cationic catalyst combinations produced significant yields of polymer with extensive incorporation of the fluorinated comonomer. These combinations are:

- 1,1,2-trifluorobutadiene-isobutylene AlBr_3
- 1,1,2-trifluorobutadiene-isobutylene- BF_3
- 1,1,2-trifluorobutadiene-methyl vinyl ether- AlBr_3

The first two combinations gave obviously low molecular weight products under the conditions used. Probably all of the molecular weights could be increased by increasing the monomer:catalyst ratio.

5. Preparation and Attempted Ring-Opening Polymerization of Fluorinated Cyclobutenes

Previous attempts to polymerize perfluorocyclobutene with catalyst systems known to polymerize cyclobutene by ring-opening⁵ were unsuccessful⁶. It seemed likely that cyclobutenes which did not have fluorine in the double bond would be more reactive than perfluorocyclobutene in this type of polymerization. Hence the lithium aluminum hydride reduction of perfluorocyclobutene was carried out under two sets of conditions to furnish the potential monomers 14 and 15.



An attempt to prepare 15 in a higher-boiling ether (1,2-diethoxyethane) to permit easier purification of 15 was unsuccessful.

The polymerizations of 14 promoted with either a TiCl₄-based catalyst or Mo or W ring-opening catalysts gave only trace yields of polymer (Table XI). If similar results are obtained with 15, this approach to fluorinated polymers will be abandoned.

6. Chemical Modification of cis-Polybutadiene

Our previous report described the preparation of an adduct of pentafluorobenzenesulfonyl chloride and cis-polybutadiene in which sufficient sulfonyl chloride was added to saturate 15% of the double bonds of the polymer⁴. A sample of this adduct has now been examined at the U. S. Army Natick Laboratories. A sulfur-cured specimen showed an R67.5 twist recovery⁷ value of -59° which is considered excellent⁸. Volume swell was found to be 122% in 70/30 isooctane/toluene.

These results suggested the preparation of adducts containing a higher proportion of fluorine to impart greater oil resistance. In addition some other addends were investigated for comparison with pentafluorobenzenesulfonyl chloride. A preliminary evaluation of these rubbery adducts has been made by us through measurement of glass transition temperature (T_g) with the aid of a Differential Thermal Analyzer. The summary of T_g data given below shows that adducts of perfluorosulfonyl chlorides (CF₃SOCl and C₆F₅SOCl) display low T_g values to a higher degree of saturation than do the corresponding perchlorosulfonyl chlorides. Adducts of C₆F₅SOCl and cis-poly-

Glass Transition Temperatures (°C.) by Differential Thermal Analysis for Adducts of cis-Polybutadiene and Sulfonyl Chlorides

<u>Addend</u>	% Saturation			
	<u>10</u>	<u>15</u>	<u>30</u>	<u>25</u>
CF ₃ SOCl	-92	-84	-75	-68
C ₆ F ₅ SOCl	-90	-80	-66	-52
CCl ₃ SOCl	-85	-50	+28	-
C ₆ Cl ₅ SOCl	-99	-50	+18	-

butadiene with 20-25% saturation will be prepared for evaluation at the U. S. Army Natick laboratories.

Another potential addend for modification of polybutadiene is nitrosyl fluoride, now available commercially as a complex $\text{NOF} \cdot 3\text{HF}$. An addition of the complex to a chloroform solution of cis polybutadiene was carried out at room temperature using 50 mole-% of the complex. An adduct of reduced solubility in heptane and low T_g (-99°) was obtained. Elemental analysis indicates the adduct contains one NOF and one HF per ten butadiene units. More of this adduct will be prepared for more complete evaluation.

EXPERIMENTAL

1. Apparatus

The vacuum line described in our earlier reports for transferring monomers to polymerization vessels was used after modification so that the mercury reservoirs for the gas measuring bulbs are covered by an argon atmosphere. These reservoirs were formerly exposed to the air.

2. Monomer Synthesis

a. 1,1,2-Trifluorobutadiene

This material was prepared in 92% yield by debromochlorination of Peninsular ChemResearch 4-bromo-3-chloro-3,4,4-trifluorobutene as described in our previous reports .

b. 1,1-Difluoroallene

A solution of 51.2 g. (0.294 mole) of 99.7% 2-bromo 3,3,3-trifluoropropene-1 (furnished by Professor Paul Tarrant) in 200 ml. of ethyl ether was cooled to -90° with liquid nitrogen and treated dropwise with 132.2 g. (0.314 mole) of 15.2% butyllithium-in-*n*-hexane and 76.7 g. of ethyl ether. The addition, carried out under a nitrogen atmosphere, required two hours at -87 to -97° . Distillation with a flash temperature up to 31° gave a total of 23.5 g. of volatile liquid product. Vpc showed the following components: 0.9% nitrogen, 0.9% carbon dioxide, 28.6% 1,1-difluoroallene, 7.0% *n*-butane, 2.8% *n*-hexane and 59.8% ethyl ether.

The higher-boiling residue was swept with nitrogen overnight to entrain 140 g. of Dry Ice-condensable liquid. Vpc of this distillate showed it to contain 3.6% of 1,1-difluoroallene.

The total yield of 1,1-difluoroallene was 53%.

c. 5,5,5-Trifluoro 4-(trifluoromethyl) 1,3-pentadiene

The precursor 1,1,1-trifluoro-2-(trifluoromethyl)-4-pentenyl 2-acetate was prepared as follows: A mixture of 124 g. (0.60 mole) of 1,1,1-trifluoro 2-(trifluoromethyl) 4-pentenol-2 (furnished by Professor Paul Tarrant, University of Florida), 183.8 g. (1.80 moles) of acetic anhydride, 56.8 g. (0.693 mole) of sodium acetate and 222.7 g. (3.71 moles) of glacial acetic acid was refluxed for five hours. The clear solution was cooled to room temperature and

stirred with 466 g. of water. A lower layer of 109 g. was separated, washed with water and dried to give 90.8 g. of crude ester, n_D^{21} 1.3332. Vpc showed this to be 75% ester, 21% unreacted alcohol and 4% unknown.

Fractionation of 89.8 g. of the crude product and 13.6 g. of trichlorobenzene in a spinning-band column gave the following fractions:

Fraction	Weight, g.	b. p., °C. (mm.)	n_D^{21}	Vpc Analysis		
				% Ester	% Alcohol	% $C_6H_3Cl_3$
1	2.9	56 (730)	1.3995	0.4	21	-
2	69.8	103-92 (500-400)	1.3485	71.3	27.7	1.0
3	13.2	84 (400-300)	1.3488	92.7	6.5	0.8
4	1.4		1.3495	96.6	3.1	0.3

These fractions constitute a 43% yield of the ester corrected to 100% purity.

A second preparation of the acetate was carried out with a seventeen hour reflux period. Isolation of the crude acetate as described above gave a yield of 86.5% of 94% pure product, n_D^{21} 1.3494.

1,1,1-Trifluoro 2-(trifluoromethyl) 4-pentenyl-2-acetate was pyrolyzed by passage through a Vycor column packed with 4-mm. glass Raschig rings and heated at 525-535° over a 22-cm. length. The rate of addition of ester to the tube and the flow of nitrogen carrier gas were adjusted to give a residence time in the heated zone of about ten seconds. The crude product was collected in a Dry Ice trap, warmed to room temperature, washed with water, dried and distilled at reduced pressure. The following fractions were collected:

Fraction	Weight, g.	b.p., °C. (mm.)	n_D^{25}	% Purity by vpc
1	9.5	38 (240)	1.3410	94.9
2	13.0	33 (200)	1.3413	93.6
3	0.8	30 (135)	1.3425	77.7
4	5.2	dry ice trap	1.3418	90.4

Fractions 1-4 represent a 62% yield of the diene corrected to 100% purity. The reported refractive index for the diene is n_D^{20} 1.3447, which may be extrapolated to 1.3422.

Anal. Calcd. for $C_6H_4F_6$: C, 37.91; H, 2.12; F, 59.97
Found: C, 38.74; H, 2.21; F, 56.93.

d. Attempted Catalytic Dehydration of 1,1,1-Trifluoro-2-(trifluoromethyl) 4-pentenol-2

A 20-mm. I. D. Vycor tube was packed for a length of 23 cm. with 70 ml. of Alcoa 6-8 mesh F-1 activated alumina. The alumina was pretreated by heating overnight at 305° under a slow stream of nitrogen. The column was then heated at 270-280° while the alcohol (23.8 g., 0.113 mole) was dropped into the column during three hours under a 50-ml./minute stream of nitrogen. The pyrolysate (13.2 g.) was condensed in a Dry Ice trap. Negligible condensate was observed in a second Dry Ice trap. Extensive char formation occurred in the heated tube. Vpc of the condensate showed the presence of 30% unreacted alcohol. No diene could be detected.

e. Attempted Phenyl Isocyanate-Promoted Dehydration of 1,1,1-Trifluoro 2-trifluoromethyl 4-pentenol-2

A mixture of 10.4 g. (0.050 mole) of the alcohol, 13.8 g. (0.115 mole) of phenyl isocyanate, 0.2 ml. of dibutyl tin dilaurate and 37.5 g. of xylene was heated overnight at 123° with stirring under a nitrogen atmosphere. After the first hour of heating, 0.41 g. (0.0044 mole) of aniline was added. No carbon dioxide evolution was noted. Volatile material (23.7 g.) swept into a Dry Ice trap during reaction was shown by vpc to contain no diene.

f. 2-(Trifluoromethyl)butadiene-1,3

3-(Trifluoromethyl) 1-butenyl 3-acetate provided by Professor Tarrant was analyzed by vpc and found to be 84.7% pure. The major contaminant was 10% of the parent alcohol. The ester (44.6 g.) was pyrolyzed under the conditions described above to give 39.5 g. of Dry Ice-condensable products. Distillation gave the following fractions:

<u>Fraction</u>	<u>Weight, g.</u>	<u>b. p., °C.</u>	<u>Diene Content (by vpc)</u>
1	3.9		67% + 32% low boiler
2	7.7	30	90%
3	10.0	50-60 (75 mm.)	0.4% + 54% HOAc

Anal. Calcd. for $C_5H_5F_3$: C, 49.19, H, 4.13

Found: C, 49.66, 59.77; H, 4.22, 4.44.

The total yield of diene was 32%.

g. 1,2-Bis(trifluoromethyl) 1,4-cyclohexadiene

The method of Putnam, Harder and Castle was used to prepare this compound from hexafluorobutyne-2 (HFB) and excess butadiene (BD) with the following results:

Run No.	HFB, g. (moles)		BD, g. (moles)		Reaction Conditions		Weight, g.	b. p., °C.	20 n_D	Yield, %
					Hrs.	°C.				
1	98	(0.602)	58	(1.07)	39	25	122.6	135	1.3783	94
2	160	(0.99)	90	(1.67)	64	25	176.7	135	1.3792	82

The products of both runs were 99.9% pure by vpc assay. The reported n_D^{25} is 1.3778.

h. Hydrogenation of 1,2-Bis(trifluoromethyl) 1,4-cyclohexadiene

This reaction was run in a model 3911 Parr hydrogenation apparatus following the procedure of Putnam, Harder and Castle. The following runs were made at 20-40 psig in a 435-ml. pressure bottle:

Run No.	Diene, g. (mole)	Start End		Other Conditions	% Hydrogen Uptake	Yield, %	19 n_D	Product		
								% Olefin Component	% Aromatic Component	% Other Components
1	97.7(.452)	0.45	0.45	Reactor cooked	34	69	1.3782	55	38	7
2	56.1(.260) ^a	0.47	0.36	Reactor not cooked	56,77,102	85	1.3753	67	10	23
3	24.5(.113) ^b	2.6	0.98	120g. THF solvent	84,93	56	1.3756	94	4	1
4	12.0(.056) ^c	0.12	0.04	-	88,91,33					

a. Added in increments of 42.5, 5.1 and 8.5 g.

b. Added in increments of 9.1 and 15.4 g.

c. Added in increments of 12, 10.9 and 20 g.

Preparative vpc of the product of run 3 gave a sample of the aromatic component whose infrared spectrum in the 2000-1600 cm^{-1} region indicated m-disubstitution.

i. Reduction of Hexafluorocyclobutene to 2,3,3,4,4-Pentafluorocyclobutene

In a 2-l. 3-necked flask were placed 1117 g. of diethylene glycol dimethyl ether (Ansul Ether 141) and 30.6 g. (0.81 mole) of lithium aluminum hydride. The mixture was cooled to -62° with stirring and treated with 100.8 g. (0.623 mole) of gaseous Peninsular ChemResearch hexafluorocyclobutene over a period of sixty-five minutes. The mixture was stirred two hours while the temperature rose to 10° and then quenched by the successive addition at $20-33^{\circ}$ of 32 ml. of water, 29.3 g. of 20% sodium hydroxide, 50 ml. of water and 30 g. of 20% sodium hydroxide. Partial distillation of the hydrolyzed product gave 38.2 g. of crude product. Redistillation through a spinning band column gave 19.0 g. (21 %) of product, b. p. $32-33^{\circ}$, n_D^{26} 1.3225. Vpc assay indicated a purity of 98.4%.

j. Reduction of Hexafluorocyclobutene to 3,3,4,4-Tetrafluorocyclobutene in Ethyl Ether Solvent

In a 2-l. flask were placed 794 g. of ethyl ether and 42.2 g. (1.11 moles) of lithium aluminum hydride. The mixture was cooled to -75° . Hexafluorocyclobutene (92.0 g., 0.568 mole) was added during 105 min. and the mixture allowed to stand 30 min. at -75° . The reaction mixture was quenched by addition of 150 ml. of water (temperature rose to -35°) and 382 g. of 46% sulfuric acid at -40° to -50° . The mixture was stirred overnight at room temperature. The lower aqueous layer was extracted twice with 100-ml. portions of ether and combined with the upper organic layer. The combined organic products were dried over magnesium sulfate and distilled through a spinning band column to give 3,3,4,4-tetrafluorocyclobutene containing some ethyl ether. Calculation from vpc analysis showed the yield of pure tetrafluorocyclobutene was 17.9 g. (25%).

k. Attempted Reduction of Hexafluorocyclobutene to 3,3,4,4-Tetrafluorocyclobutene in 1,2-Diethoxyethane Solvent

In a 2-l. three-necked flask were placed 602 g. of 1,2-diethoxyethane (Eastman Kodak) and 29.2 g. (0.77 mole) of lithium aluminum hydride. The mixture was cooled to -70° . Hexafluorocyclobutene (98.1 g., 0.605 mole) was added at -70 to -72° over a period of ninety-five minutes.

The reaction mixture was allowed to stand another thirty minutes at -70° and then was treated with a solution of 117 g. of n-butanol and 21 g. (1.17 mole) of water. This addition required ten minutes and produced a slight exotherm. Excess water (125 g., 7 moles) was added. As the mixture was warmed to -40° an exotherm to 60° occurred with some loss of volatile products. The reaction mixture was acidified with 100 ml. of sulfuric acid in 200 ml. of water and stirred overnight at room temperature under a slow stream of nitrogen. Passing the nitrogen stream through a Dry Ice trap condensed 42 g. of volatile product of which 13 g. boiled below room temperature. Vpc of both fractions showed little if any product of the $C_4H_5F_5$ or $C_4H_2F_4$ type, nor could any be found upon distillation of the acidified hydrolysis residue.

3. Catalyst Synthesis

Nickel (0) Bis(1,5-cyclooctadiene)

A Soxhlet extraction apparatus was assembled with 12.85 g. (0.050 mole) of nickel (II) acetylacetonate in a 20 x 80-mm. thimble and a boiling flask containing 72 ml. (63.4 g., 0.86 mole) of 1,5-cyclooctadiene, 25.25 ml. (19.9 g., 0.100 mole) of aluminum triisobutyl and 150 ml. of ether. After refluxing the ether solution in the boiling flask for twenty-four hours there remained 3.8 g. of nickel (II) acetylacetonate in the thimble. Large yellow crystals of nickel (0) bis(1,5-cyclooctadiene) had formed in the flask. The mixture was chilled in an ice-water mixture and the liquid drawn off. The residue was washed with 10 ml. of ether and dissolved in 100 ml. of dry benzene to give a catalyst solution found to be effective in causing polymerization of allene.

X-ray fluorescence analysis of the catalyst solution showed the yield to be 5 g. or 52% based on nickel (II) acetylacetonate used.

4. Polymerizations

Polymerizations have been carried out by the procedure described in our first report. When a catalyst derived from two or more components is used, the general practice is to form the catalyst by mixing components in the presence of monomer. This technique has often been found to produce a more active catalyst than is obtainable by premixing catalyst components.

5. Addition of Nitrosyl Fluoride-Hydrogen Fluoride (NOF-3HF) to cis-Poly(butadiene)

A solution of 6.55 g. (0.121 mole) of Phillips cis-poly(butadiene) in 145.7 g. of n-heptane was placed in a polyethylene bottle and diluted with 337 g. of reagent chloroform and treated with 6.30 g. (0.0575 mole, 0.475 equiv.) of Ozark-Mahoning NOF·3H₂O . The bottle was closed and the mixture was stirred overnight at room temperature. A slight pressure rise was noted. An insoluble solid (0.75 g.) was removed. A 94-g. aliquot of the reaction mixture was stirred into 1200 ml. of n-heptane to precipitate 1.10 g. of brown rubber.

Anal. Calcd. for [(C₄H₆)₁₀NOF·HF]_n: N, 2.30; F, 6.24

Found: N, 2.66; F, 6.37

A 210-g. aliquot of the reaction mixture was stirred into methanol to precipitate 2.78 g. of brown rubber of Tg -99°.

PROPOSED WORK

1. Continue screening new fluoromonomers such as

1,1,2-Trifluoro-3-(trifluoromethyl)butadiene
1,1,2-Trifluoro-4-(trifluoromethyl)butadiene
3,3,3-Trifluoropropene
 α -(Trifluoromethyl)-2,3,4,5,6-pentafluorostyrene
1,1,2,3-Tetrafluoro-3-vinylcyclobutane
3,3,3-Trifluoro-2-(trifluoromethyl)propene

with new catalysts (anionic, cationic, anionic coordination) in homopolymerization and copolymerization. Major effort will be with the conjugated dienes having double bonds of approximately equal reactivity.

2. Continue studies of effect of feed ratio on combined monomer ratio in various types of polymerizations.

3. Scale-up the preparation and polymerization of the more promising monomers to overcome some of the difficulties inherent in small-scale polymerization and to provide polymers for evaluation.

4. Prepare adducts of unsaturated rubbers, such as cis-poly(butadiene), and trifluoromethanesulfonyl chloride, pentafluorobenzene sulfonyl chloride or nitrosyl fluoride hydrofluoride in larger quantities and at higher levels of saturation for evaluation at U. S. Army Natick.

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Table I
Polymerization of 1,1-Difluoroallene

<u>Reagent</u> ^a	<u>Experiment No.</u>			
	<u>85-1</u>	<u>85-2</u>	<u>85-3</u>	<u>85-4</u>
(1) Azobisisobutyronitrile, g.	0.01	-	-	-
(2) 2.2% Ether solution of difluoroallene, ml.	37	37	37	37
(3) 1.37 M t-butyl MgCl in MgCl in THF, ml.	-	-	1	-
(4) 47% BF ₃ etherate, ml.	-	-	-	0.25
Polymerization temperature, °C.	50	50	50	-80
Polymerization time, hrs.	167	167	18	167
Appearance of reaction tube at end of reaction	clear solution	clear solution	white precipitate	clear solution
Yield, g.	0.320	0.122	0.024	0.126
Appearance of polymer	white grease	white grease	trace brown grease	white soft resin

a. Reagents (1)-(2) charged to tube; tube 85-4 cooled to -78°; reagents (3)-(4) added; polymerizations run as indicated.

Table II
Copolymerization of Allene and 1,1-Difluoroallene

Reagent ^a	Experiment No.						
	87-1	87-2	87-3	87-4	87-5	87-6	87-7
(1) Benzene, ml.	5	5	5	5	-	-	-
(2) Heptane, ml.	-	-	10	-	5	5	5
(3) 0.18 M Ni(O)(COD) ₂ in C ₆ H ₆ , ml.	1	1	1	-	-	-	-
(4) 0.25 M Tetrabutyl titanate in C ₆ H ₆ , ml.	-	-	-	2	-	-	-
(5) 0.05 M VOCl ₃ in heptane, ml.	-	-	-	-	4	4	4
(6) 5-8% Difluoroallene in ether + heptane, ml.	8.8	8.8	-	8.8	8.8	8.8	-
Color					dark red brown	red brown	greenish
Coolant	-	CO ₂	CO ₂	-	-	liq. N ₂	CO ₂
(7) Allene, mmoles	-	25	25	-	-	25	25
(8) 1.25 M Al(<i>i</i> -Bu) ₃ , ml.	-	-	-	2	1.67	1.67	1.67
Polymerization time, hrs.	22	22	22	99	99	99	99
Appearance of polymerizing mixture	orange ppt.	ppt. + yellow soln.	ppt. + yellow soln.	brown susp.	brown susp.	black susp.	gelled at once, white ppt.
Yield, g.	.526	1.326	.171	.254	.054	0.162	1.390
Conversion, %	81	81	17	39	8	10	139
Resin appearance	white	brown	grey brown	light brown	light brown	light buff	light gray

a. Reagents (1)-(6) charged to tubes; colors noted as shown; tubes chilled in Dry Ice or liquid nitrogen as indicated; allene distilled in; mixtures stirred to homogeneity at 5°; reagent (8) added; tubes 87-4 to 87-7 shaken 15 minutes at 25°; all polymerizations run at 50°.

Table III

Evaluation of Catalyst Activity in Copolymerization of Ethylene and Butadiene. Copolymerizations of 25 mmoles of each monomer (2.05 g. total monomer weight).

Reagent ^a	Experiment No.					
	75-1	75-2	75-3	75-4	75-5	75-6
(1) Heptane, ml.	9	9	8	7	10	9
(2) Benzene, ml.	8	8	8	7	-	-
(3) .55M Al(<i>i</i> -Bu) ₃ , ml.	0.4	0.5	-	-	-	-
(4) .06M Co Octoate, ml.	-	-	1	-	-	-
(5) .25M BuVanadate, ml.	-	-	-	2.0	-	-
(6) .017M TiI ₄ , ml.	-	-	-	-	7.85	8.6
(7) .5M TiCl ₄ , ml.	0.4	0.4	-	-	-	-
(8) .3M Et ₃ Al ₂ Cl ₃ , ml.	-	-	1	-	-	-
(9) 1.25M Al(<i>i</i> -Bu) ₃ , ml.	-	-	-	2	0.54	0.54
Polymer Yield, g.	0	0.755	0.512	0.243	0.683	0.949
Polymer Infrared Analysis	-	Not fully interpretable, but cannot be high vinyl.	72% cis 19% vinyl or 9% trans No P.E. crystallinity at 730-720 cm ⁻¹ .	40% cis -CH ₂ -CH ₂ - 33% vinyl 22% trans some P.E. crystallinity.	-	75% cis or -CH ₂ -CH ₂ - 3.5% vinyl 19% trans strong P.E. cryst. 720-730 band is wide, indicating cis-polybutadiene.

- a. Reagents (1)-(6) charged to reaction tubes; tubes chilled in liquid nitrogen; monomers distilled in; tubes pressurized to 4 psig with nitrogen, warmed and shaken at -50° to give homogeneous system at low pressure; reagents (7)-(9) added; tubes shaken 15 minutes at 5° and polymerizations run 16 hours at 5°.

Table IV
Copolymerizations of Butadiene and 1,1,2-Trifluorobutadiene

Reagent ^a	Experiment No.							
	79-1	79-2	79-3	79-4	79-5	79-6	79-9	79-10
(1) Heptane, ml.	8	8	9	9	7	7	9	9
(2) Benzene, ml.	8	8	-	-	7	7	8	8
(3) 0.06 M Co Octoate, ml.	1	1	-	-	-	-	-	-
(4) 0.017 M TiI ₄ , ml.	-	-	8.6	8.6	-	-	-	-
(5) 0.25 M Bu Vanadate, ml.	-	-	-	-	2.0	2.0	-	-
(6) 0.55 M Al(<i>i</i> -Bu) ₃ , ml.	-	-	-	-	-	-	0.5	0.5
(7) Butadiene, mmoles	36	40	36	40	36	40	36	40
(8) Trifluorobutadiene, mmoles	14	10	14	10	14	10	14	10
(9) 0.3 M Et ₃ Al ₂ Cl ₃ , ml.	1	1	-	-	-	-	-	-
(10) 1.25 M Al(<i>i</i> -Bu) ₃ , ml.	-	-	0.54	0.54	2.0	2.0	-	-
(11) 0.5 M TiCl ₄ , ml.	-	-	-	-	-	-	0.4	0.4
Yield, g.	0.273	0.011	0.14	0.747	0.062	0.031	0.209	0.071
Conversion, % ^b	8	0.03	4	23	2	1	6	2

a. Reagents (1)-(6) charged to reaction tubes, tubes chilled in Dry Ice; monomers distilled in; tubes pressurized to 4 psig with nitrogen, warmed and shaken at 5°; reagents (9)-(11) added; tubes shaken 15 minutes at 5° and polymerizations run 19 hours at 5°.

b. Based on total weight of monomers used.

Table V

Terpolymerization of Ethylene, Butadiene and 1,1,2-Trifluorobutadiene

Reagent ^a	<u>Experiment No.</u>					
	<u>77-1</u>	<u>77-2</u>	<u>77-3</u>	<u>77-4</u>	<u>77-5</u>	<u>77-6</u>
(1) Heptane, ml.	9	9	9	9	9	9
(2) Benzene, ml.	8	8	8	-	-	-
(3) 0.5 M TiCl_4 , ml.	0.4	0.4	0.4	-	-	-
(4) 0.017 M TiI_4 , ml.	-	-	-	7.85	8.6	8.6
(5) $\text{CF}_2=\text{CF}-\text{CH}=\text{CH}_2$, mmoles	12.5	7.5	7.5	7.5	7.5	12.5
(6) Butadiene, mmoles	25	35	35	35	35	25
(7) Ethylene, mmoles	12.5	7.5	7.5	7.5	7.5	12.5
(8) 0.55 M $\text{Al}(\text{i-Bu})_3$, ml.	0.5	0.5	0.6	-	-	-
(9) 1.25 M $\text{Al}(\text{i-Bu})_3$, ml.	-	-	-	0.54	0.54	0.54
Yield, g.	0.022	0.478	0.278	0.636	1.046	0.692
Conversion, % ^b	0.7	16	10	22	36	23
Infrared ^c	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $\left\{ \begin{array}{l} \text{buff crumb} \\ \text{homogeneous} \end{array} \right\}$ </div> <div style="text-align: center;"> $\left\{ \begin{array}{l} \text{light brown rubbers} \\ \text{white resins} \end{array} \right\}$ </div> </div>					
	-	No F	No F	trace F	trace F	trace F
Main component	<u>ethylene</u> <u>ethylene</u> <u>cis butadiene</u>					

- a. Reagents (1)-(4) charged to tubes; tubes frozen in Dry Ice, evacuated, frozen in liquid nitrogen; monomers distilled in; tubes pressurized with 4 psig nitrogen, warmed to -50° ; reagents (8)-(9) added; tubes shaken 15 minutes at 5° and polymerizations run 20 hours at 5° .
- b. Based on total weight of monomers used.
- c. Of rubbery product.

Table VI
Polymerizations of 5,5,5-Trifluoro-4-(trifluoromethyl)-
1,3-butadiene

<u>Reagent</u>	<u>Experiment No.</u>					
	<u>81-1</u>	<u>81-2</u>	<u>81-3</u>	<u>81-4</u>	<u>81-5</u>	<u>81-6</u>
Benzene, ml.	16	16	16	9	9	6
TiI ₄ , mmols	0.2	-	-	-	-	-
Co Octoate, mmols	-	0.06	-	-	-	-
VOC1 ₃ , mmols	-	-	0.5	-	-	-
Ti(OBu) ₄ , mmols	-	-	-	0.5	0.5	-
TiCl ₄ , mmols	-	-	-	-	-	0.5
(CF ₃) ₂ C=CH-CH=CH ₂ , mmols	24	24	12	12	6.9	<3.4
Butadiene, mmols	25	25	-	-	-	-
Al(<i>i</i> -Bu) ₃ , mmols	1	-	-	2.5	-	1.5
Et ₃ Al ₂ Cl ₃ , mmols	-	0.3	1.25	-	-	-
Decyl Mg Iodide, mmols	-	-	-	-	1.5	-
Polymerization temperature, °C.	50	50	25,50	25,50	25,50	25,50
Polymerization time, hrs.	40	40	18,24	18,24	18,24	18,24
Yield, g.	0.976 Yellow oil	0.135 White gum	0.018	0.158	0.005	0.034
Conversion, % ^a	16.5	2.3	0.8	6.9	0.4	>5

a. Based on total weight of monomers used.

Table VIII

Ionic Polymerizations of 2,2,2-Trifluoroethyl Vinyl
Ether and 1,1,2-Trifluorobutadiene

<u>Reagent</u>	<u>Experiment No.</u>							
	<u>80-1</u>	<u>80-2</u>	<u>80-3</u>	<u>80-4</u>	<u>80-5</u>	<u>80-6</u>	<u>80-7</u>	<u>80-8</u>
Tetrahydrofuran, ml.	10	10	10	10	10	10	-	-
Benzene, ml.	-	-	-	-	-	-	10	-
CH ₂ Cl ₂ , ml.	-	-	-	-	-	-	-	8.6
CF ₃ CH ₂ OCH=CH ₂ , mmoles	24	24	24	-	-	-	-	-
1,1,2-Trifluorobutadiene, mmoles	-	-	25	25	25	25	25	25
LiBu, mmoles	1	1	1	1	-	-	1	-
<i>t</i> -Butyl MgCl, mmoles	-	-	-	-	2	2	-	-
AlBr ₃ , mmoles	-	-	-	-	-	-	-	0.1
Polymerization temperature, °C.	25	50	25	50	25	50	50	-80
Time, hrs.	89	89	89	89	89	89	89	0.5
Yield, g.	0.009	-	0.096	0.271	0.372	0.199	0.049	0.029
Conversion, % ^a	0.3	-	1.7	10	14	7	2	1
Polymer appearance	gummy white resin	- - -	white bits of film	light brown film	tan lumps	tan lumps	white crumbs	tan lumps

a. Based on total weight of monomers used.

Table IX

Copolymerizations of 1,1,2-Trifluorobutadiene Initiated by Cationic Catalysts

Reagent	Experiment No.							
	73-2	73-3	73-4	73-5	73-6	73-7	73-8	73-9
CH ₂ Cl ₂ , ml.	10	10	10	10	10	10	10	10
Butadiene, g.	4.58	4.87	-	-	-	-	-	-
CF ₂ =CF·CH=CH ₂ , g.	1.82	3.21	1.82	1.82	1.82	1.82	1.82	1.82
Isobutylene, g.	-	-	5	4.88	-	-	-	-
Isoprene, g.	-	-	-	-	2.70	2.78	-	-
Methyl vinyl ether, g.	-	-	-	-	-	-	3.09	-
α-Trifluoro vinyl ether, g.	-	-	-	-	-	-	-	4.64
0.1 M AlBr ₃ , ml.	1	-	1	-	1	-	1	1
47% BF ₃ etherate, ml.	-	0.25	-	0.25	-	0.25	-	-
Yield, g.	0.15	4.43	2.45	2.51	0.18	2.38	0.72	trace
Conversion, % ^a	2.3	55	36	37	4	52	18	-
Polymer appearance	white resin	white resin	semi-fluid	semi-fluid	white resin	white resin	stiff rubber	-
% F	-	2.64	4.12	4.23	3.22	1.65	12.87	-
% CF ₂ =CFCH=CH ₂ in product	-	5.01	7.83	8.03	6.11	3.13	24.4	-
F monomer/other monomer in product	-	.0527	.0849	.0874	.0652	.1323	.322	-
F monomer/other monomer in feed	-	.66	.364	.373	.675	.655	.589	.394
Ratio $\frac{\text{F monomer in product}}{\text{F monomer in feed}}$	-	.08	.23	.23	.010	.05	.55	-

a. Based on total weight of monomers used.

Table X
Lithium Butyl-Initiated Copolymerizations of 1,1,2-
Trifluorobutadiene and Butadiene

Reagent	Experiment No.						
	86-1	86-2	86-3	86-4	86-5	86-6	86-9
Benzene, ml.	15	-	-	-	-	-	-
Tetrahydrofuran, ml.	-	15	15	15	15	15	15
Butadiene, mmoles	25	25	25	12.5	37.5	25	12.5
1,1,2-Trifluorobutadiene, mmoles	25	25	25	37.5	12.5	25	37.5
Homogenize at 25°	Yes	Yes	Yes	-	Yes	Yes	-
Add catalyst at -80°	-	-	-	Yes	-	-	Yes
.16 M Lithium Butyl, ml.	1.0	1.0	.5	.5	.5	-	.5
Polymerization Temp., °C.	50°	25°	50°	50°	50°	50°	50°
Polymerization Time, hrs.	69	69	69	69	69	143	67.5
Appearance during polymerization	red brown	yellow brown	yellow brown	-	-	clear	-
Yield, g.	.061	.033	.033	<.104	.035	.136	<.162
Conversion, % ^a	1.5	.8	.8	<2.2	<1.0	3.4	<3.4
Appearance	< brown	rubber	>	black rubber	trans-parent rubber	brown rubber	

a. Based on total weight of monomers used.

Table XI

Attempted Polymerizations of 2,3,3,4,4-Pentafluorocyclobutene

<u>Reagent</u> ^a	<u>Experiment No.</u>		
	<u>76-1</u>	<u>76-2</u>	<u>76-3</u>
(1) MoCl ₅ , g.	.142	-	-
(2) WCl ₆ , g.	-	.198	-
(3) 0.5 M TiCl ₄ in benzene, ml.	-	-	1
(4) Dry Benzene, ml.	20	20	20
(5) 2,3,3,4,4-Pentafluorocyclobutene, ml.	2.5	2.5	2.5
(6) 1.25 M Al(<u>i</u> -Bu) ₃ , ml.	1.2	1.2	1.2
Yield	Trace brown scum in all on wall of beaker after work-up		

- a. Reagents (1)-(5) placed in tube; tube sealed and agitated to give solution, then chilled to 5°; reagent (6) added; mixture stirred 15 minutes at 5°; polymerization run 94 hours at 5°.

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c.	8b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) 67-58-CA		
d.			
10. AVAILABILITY/LIMITATION NOTICES Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY U. S. Army Natick Laboratories Natick, Mass.	
13. ABSTRACT Catalyst and fluorinated-monomer combinations were screened for activity in homopolymerization and copolymerization. Copolymerizations of fluorinated dienes with butadiene or ethylene and butadiene were studied using both coordination and ionic catalysts. Preliminary studies were made of the relation of feed ratio to combined monomer ratio in some of these polymerizations. The additions of sulfenyl chlorides and of nitrosyl fluoride-hydrogen fluoride complex (NOF·3HF) to <u>cis</u> -polybutadiene were studied.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
POLYMERIZATION						
FLUORO-OLEFINS						
COPOLYMERIZATION						
TRANSITION METALS						
CATALYSIS						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

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8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

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Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
POLYMERIZATION	8		8			
FLUORO-OLEFINS						
COPOLYMERIZATION						
TRANSITION METALS						
CATALYSIS						
Fluorochemicals	1,2		1,2			
High-strength	0		0			
Elastomers	2		2			
Resistance	4		4			
Chemical properties	4					
Temperature						

INSTRUCTIONS 4

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